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Rapid production of cadmium infinite coordination polymer nanofiber via solvent induced precipitation method

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ABSTRACT

The precipitation synthesis of cadmium infinite coordination polymer (Cd-ICP) nanofibers with a high degree of uniformity is reported. The elemental analyses (CHN and ICP-OES), energy-dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA) show that thermally robust monodisperse solid consists of bi-carboxylic acid linker and cadmium ion. The coordination between the Cd^{2+} ion and bi-carboxylic acid linker was investigated by Fourier transform infrared (FT-IR) spectroscopy. The photoluminescence (PL) properties of the Cd-ICP were studied in comparison with those of the bi-carboxylic acid linker. It was shown that the emission intensity of the Cd-ICP is much stronger than linker due to the structural rigidity after the coordination of linker to Cd ions. The field emission scanning electron microscopy (FE-SEM) results show that after calcination of the Cd-ICP the morphology changed from fiber to hexagonal-like disc. Furthermore, the results of UV–Vis spectroscopy show larger band gap for obtained CdO relative to the bulk counterpart.

1. Introduction

Metal–organic frameworks (MOFs) and infinite coordination polymers (ICPs) exhibit a high level of structural tailorability [1–5]. The rich coordination chemistry of metal ions with multidentate ligands offers versatility from both structural and functional aspects [6–8]. The molecular structures of the formed complexes dictate the formation, organization, and function of discretely defined assemblies at the micrometer scale. In addition, the applied assembly process and reaction parameters also play key roles [9]. Fundamental research resulted in the formation of functional metal–organic materials [10,11], some of which have already been developed into commercially available products. In 2005, by simply adding an initiation solvent to a precursor solution containing metal ions and ligands, spherical infinite coordination polymer nanoparticles were obtained firstly by Mirkin group [12], Dong and Wang group [13], independently.

Recently, the photoluminescence properties of the coordination polymers, especially those based on the d^{10} metals, Lanthanides (4f) or the d^{10}-4f hetero metals, have attracted great attention of the researchers [14–16]. Controlling optical properties of coordination polymers is possible through the choice of starting materials (metal and ligand precursors), ancillary ligands and post-modification processes. Mirkin reported that adding different solvents to a dispersion of ICP particles enables adjusting the optical properties of these particles [5,12]. Since the size of these particles and their corresponding optical properties can be easily controlled, they may serve as a new class of diagnostic labels for various detection applications.

CdO is an important II–VI semiconductor and the preparation of CdO nanostructures has received much attention for various optoelectronic devices due to its high electrical conductivity (even without doping), high carrier concentration, and high optical transmittance in the visible region of the solar spectrum [17–19]. CdO has a narrow direct band gap ranging from 2.2 to 2.5 eV and an indirect band gap of 1.98 eV [20]. The different band gap is attributed to cadmium and oxygen vacancies and strongly depends on the fabrication procedures [21]. CdO nanostructures have been fabricated by various techniques such as pulsed-laser deposition [22], magnetron sputtering [23], sol–gel [24], metal–organic chemical vapour deposition [25], and hydrothermal methods [26]. Recently, a facile fabrication method has been used to convert the coordination polymer nanostructures into metal oxides with similar morphology by thermal treatment [15,27–30].

Regardless of the remarkable recent progress in this field, it is still a challenge to design MOFs, ICPs, and related materials with a desired structure and function based on a given set of metal complexes and ligands. For example, the bottom-up assembly of coordination-polymer nanofibers from multidentate ligand and metal salt is largely unexplored. In this work, we use bi-carboxylic acid ligand and Cd^{2+} to obtain fluorescent cadmium coordination polymer. Appropriate thermal treatment conditions were used to fully convert Cd-ICP to CdO.

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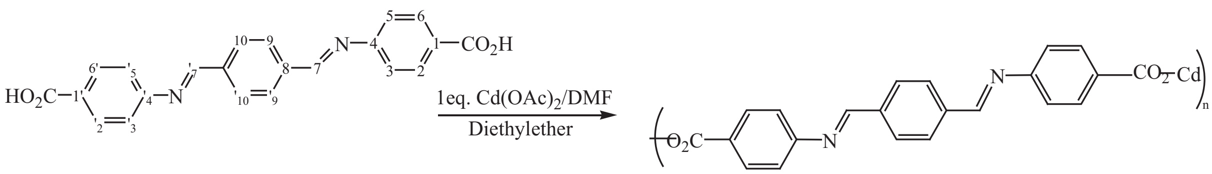

Fig. 1. Coordination polymerization used to obtain ICP particles (schematic).

2. Experimental

2.1. Materials and Apparatus

Solvents and all other chemicals were obtained from commercial sources and used as received unless otherwise noted. The ligand precursor 4,4′-((1E,1′E)-(1,4-phenylene bis(methanylylidene)) bis (azanylylidene)) dibenzoic acid was synthesized according to the published methods [30].

The CHN elemental analyses were done by Perkin-Elmer 2400 SERIES II. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted on ICP-OES 730-ES, Varian. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Electrospray ionization mass spectrometric (ESI-MS) spectrum was obtained on a

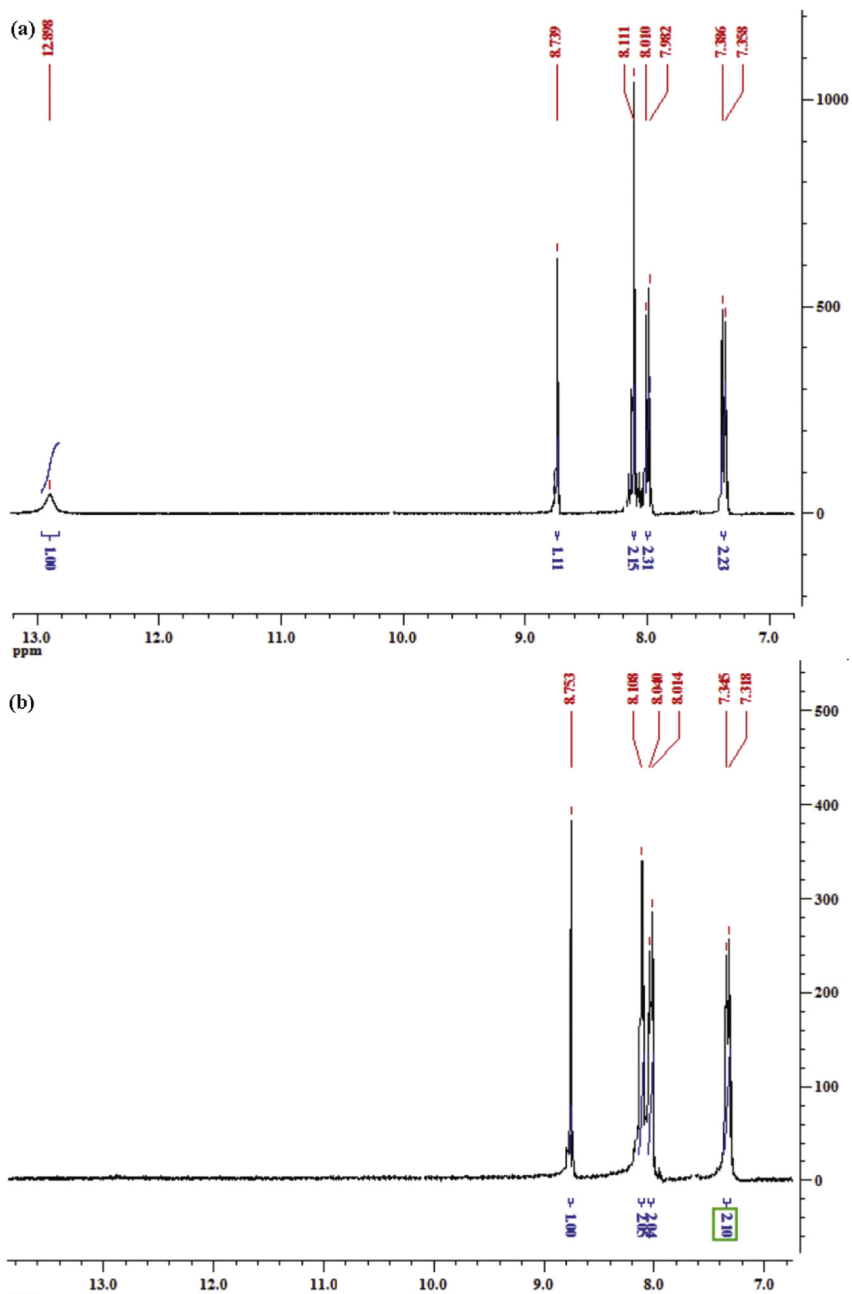

Fig. 2. ^{1}HNMR spectra of (a) ligand and (b) Cd-ICP.